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Positive Ion-Molecule Reactions in OCS/Hydrocarbon Mixtures

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Abstract

The positive ion-molecule reactions of OCS have been investigated
in an ion cyclotron resonance spectrometer. A variety of reactions
in OCS/hydrocarbon mixtures have been investigated for C_1-C_4 hydro-
carbons which are alkanes, alkenes and alkynes. The formation of organo-
sulfur ions is found in reactions in OCS/hydrocarbon (C_n) mixtures
with n<4. Formation of organo-sulfur ions is observed from hydrocarbon
ions reacting with OCS and OCS^+ and S^+ reacting with the hydrocarbons.
The proton affinity of OCS has been determined to be 168±5 kcal/mol
while that of CS_2 is measured to be 179±3 kcal/mol. Comparison with
the proton affinity of CO_2 shows that the proton affinity increases as
sulfur is substituted for oxygen.

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Introduction

The chemistry of OCS has recently been studied in an RF discharge-generated plasma.[1] Because of the paucity of available data on the ion-molecule reactions of sulfur-containing compounds, especially those of OCS^+ and S,[+2-4] it was difficult to ascertain which chemical processes in the plasma were due to the reactions of free radicals and which were due to the reactions of ions, especially when hydrocarbon scavengers were introduced. We have thus studied the ion-molecule chemistry of OCS with a variety of hydrocarbons in an ion cyclotron resonance (ICR) spectrometer. This provides a complement to the earlier mass spectrometric studies.

Experimental

These studies were performed on a modified Varian V-5900 ICR spectrometer.[5] Experiments were performed at a fixed frequency (usually 153.5 or 307.1 KHZ) and with a variable field (0-13KG). A rectangular cell operated in the drift mode was employed. Such instrumentation has previously been described in detail.[6] Total operating pressures were in the range of $2-6\times10^{-5}$ torr as measured by a Varian UHV nude ionization gauge. The pressure ratios of OCS: hydrocarbon were varied in the range 1:1 to 3:1. Under a pressure ratio of OCS:hydrocarbon of 6:1 the ion-molecule reactions of hydrocarbon ions with neutral OCS were studied for methane as the reagent gas. Ionization energies ranged from 20 to 50 eV. We note that the OCS can have a deleterious effect on the operating characteristics of the filament. This is presumably due to poisoning of the filament due to the presence of the sulfur. All reactions were confirmed by double resonance

experiments. Double resonance experiments were performed by sweeping the frequency of a second oscillator applied to the analyzer region of the cell. Typical double resonance rf voltages ranged from 10-80 mv peak-to-peak. All compounds employed in these experiments were obtained from commercial sources and were degassed by freeze-pump-thaw cycles.

Heats of formation for most ions and nonradical neutrals were taken from a standard compilation.[7] The values for the alkyl cations from Ref. 7 are in good agreement with a recent photo-ionization study.[8] Heats of formation for various radicals not in Ref. 7 were taken from Ref. 9 and 10 while values of ΔH_f's for the alkynes were taken from Ref. 11. Values of ΔH_f for many organosulfur ions were taken from electron-impact spectroscopy.[12,13] The heat of formation for CH_3S^+ has been obtained from a collisional activation and theoretical study[14a,b] and from ion cyclotron resonance spectroscopy.[14c] The heat of formation of HCS^+ was taken from a theoretical study.[15] Values of ΔH_{Rxn} that are uncertain are marked by an asterisk.

Results and Discussion

Pure OCS

The ion-molecule chemistry of pure OCS is quite simple and the important reactions together with calculated values for ΔH are given in Table 1. The two most important reactions are the reaction of the parent to form CS_2^+ and the reaction of S^+ to form S_2^+. The ion S_2^+ can also be formed from the reaction of the parent ion even though this reaction is calculated to be slightly endothermic. Dzidic et al[3] observed reactions (2)

and (3) in a high pressure mass spectrometer experiment and demonstrated
that reaction (2) is occurring because the appearance potential of S_2^+
is the same as that of OCS^+. Praet and Delwiche[4] have reported
the presence of reactions 1 and 2 in a high pressure mass spectrometer.
Reaction 3 has been studied by Matsumoto et al[3] for both ground and
excited state S^+ ions. Comparison with Table 1 of Reference 1 shows
that the condition in the icr are most like the low pressure, low power
conditions in the plasma. However, even for the lowest operating conditions in the
plasma, the ion S_3^+ is observed. At the highest pressure studied in the icr,
8×10^{-5} torr, no S_3^+ ion was observed.

Proton Affinity of OCS

An ion that is formed in many OCS/hydrocarbon mixtures is m/e = 61,
$HCOS^+$. We have examined a number of proton transfer reactions involving
$HCOS^+$ in order to determine the proton affinity, PA, of OCS. The proton
affinity was determined by the bracketing technique.[17] The proton affinity
of OCS was found to be between that of C_2H_4(PA = 163.5 kcal/mol)[18] and that
of H_2O(PA = 173.0 kcal/mol)[18] giving a value of 168±5 kcal/mol for PA(OCS).
In order to form reasonable amounts of protonated parents, CH_4 (or CD_4) was
added as a proton source.

In order to provide a comparison of the proton affinities for the series
CO_2, COS and CS_2, we have also determined the value of PA(CS_2), again by the
bracketing technique. The value for PA(CS_2) falls between that of propyne,
PA = 182 kcal/mol,[18] and H_2S, PA = 176.6 kcal/mol,[18] giving PA(CS_2) = 179±3
kcal/mol. The value for PA(CO_2) is 126.8 kcal/mol[18] and, thus, the proton

affinities increase in the order $PA(CO_2) < PA(COS) < PA(CS_2)$. A simple explanation for this trend can be found in the trends in the ionization potentials, $IP(B)$ (Table 2). The proton affinity $PA(B)$, and the $IP(B)$ on a given base are related by the following thermodynamic relationship

$$PA(B) = IP(H^+) - IP(B) + HA(B)$$

where HA is the hydrogen affinity of the base defined as $-\Delta H$ for the reaction $B^+ + H \rightarrow HB^+$. The thermodynamic values are summarized in Table 2.[7,18] From these values, it can be seen that the most important feature in determining the changes in $PA(B)$ is the decrease in $IP(B)$ as sulfur is substituted for oxygen.

In contrast, the proton affinities for the diatomics CO[18] and CS[15,16] are determined by a large cancellation between the values of $IP(B)$ and $HA(B)$. This leads to values for ΔPA between CO_2 and COS that are comparable to those between CO and CS.

<u>OCS/Alkanes</u>

In Table 3, we show the reactions observed in mixtures of OCS with various alkanes. The reactions of OCS^+ with CH_4 leads to the formation of CH_3S^+ and CHS^+ ions. The neutral products should be HCO and $HCO + H_2$ respectively. The OCS^+ ion also forms CH_3CO^+ ion and HS upon reacting with CH_4. Therefore both CO and S transfer coupled with hydride abstraction occurs. The S^+ ion reacts with CH_4 forming CH_3S^+ and a hydrogen atom. The hydrocarbon ion CH_3^+ undergoes a CO elimination reaction with OCS to form CH_3S^+, 8. Reaction 8 has also been observed by Dzidic et al.[2] in CH_3I/OCS mixtures. If the reported literature values for $\Delta H_f(CHS^+)$[13b,15,16] and $\Delta H_f(CH_3S^+)$[14c] are employed, then both reactions (4) and (5) are endothermic. Kebarle and coworkers[2] have also

observed these endothermic reactions and we suggest that the values for ΔH_f are slightly too high for these ions. The CH_3^+ ion can undergo CO addition to form CH_3CO^+ and S neutral. Using deuterated methane, we observed the formation of $DOCS^+$ via deuteron transfer from CD_5^+ and CD_4^+, reactions 10 and 11. (Reaction 11 may not occur if the double resonance is a result of the ion-molecule reaction of CD_4^+ with CD_4 to form CD_5^+ and CD_3.) The reactions observed in the methane/OCS mixture are similar to those observed by McAllister for the methane/CS_2 mixture,[19] using ICR spectroscopy. He observed the following reactions

$$CS_2^+ + CH_4 \rightarrow CH_3S^+ + HCS \qquad (4')$$

$$\rightarrow CH_3CS^+ + HS \qquad (6')$$
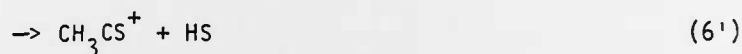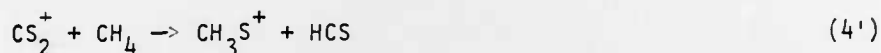
which are the sulfur analogs of Reactions 4 and 6.

The reactions of OCS^+ with C_2H_6 are somewhat different from those observed for CH_4. The transfer of S^+ to C_2H_6 from OCS^+ occurs leading to the formation of $C_2H_6S^+$ and CO, consistent with the observations of Dzidic et al. who employed C_2D_6 in their study. OCS^+ can also transfer CO^+ while the sulfur abstracts a hydrogen to form $C_2H_5CO^+$ and HS, which is similar to reaction 6 in the OCS/CH_4 mixture. The $C_2H_5CO^+$ ion was not observed by Dzidic et al.[2] although the $C_2H_2S^+$ ion was observed in their work and not in our study. The reaction of S^+ with C_2H_6 is simply a hydride abstraction to form $C_2H_5^+$ and neutral HS. As found for the reactions of CH_3^+ and $C_2H_5^+$ with OCS (8 and 17 respectively), $C_2H_6^+$ reacts with OCS abstracting S^+ to form $C_2H_6S^+$ and CO. The $C_2H_5CO^+$ ion is also a product of the reaction of $C_2H_6^+$ and OCS. Again, reaction 16 was not observed by Dzidic et al.[2]

The reactions of OCS and higher alkanes than C_2H_6 are complicated by the presence of the charge transfer channel $OCS^+ + R \rightarrow OCS + R^+$ which is now exothermic. Formation of $C_3H_7^+$ is observed in OCS/propane mixtures. This reaction is approximately thermoneutral only if the neutral products are HS and CO (rather than H and OCS) and if the ion is the stable 2-propyl cation. No other reactions of OCS^+ are observed. The only reaction of S^+ with propane is hydride abstraction. (The adduct ion $C_3H_8S^+$ cannot be observed due to the presence of the CS_2^+ peak. Pressure dependence studies of m/e = 76 suggest that no adduct ion is observed). In OCS/n-butane mixtures, the formation of $C_4H_9^+$ is observed as well as $C_3H_7^+$. Formation of $C_4H_9^+$ from n-butane can lead to either HS and CO or H and OCS as neutral products on thermodynamic grounds. This is based on the assumption that the $C_4H_9^+$ is the t-butyl cation. We prefer the former channel following the reactions of OCS^+ with propane. Formation of $C_3H_7^+$ occurs most likely by decomposition of the $C_4H_{10}^+$ ion after charge transfer from OCS^+ to the butane giving CH_3 and OCS as the neutral products. Based on thermodynamics, the $C_3H_7^+$ ion must form as the 2-propyl cation. For the reaction of S^+ with n-butane, both hydride and methide abstraction are observed. For OCS/isobutane mixtures, essentially the same reactions as observed in OCS/n-butane mixtures are found.

OCS/Alkenes

The reactions that occur in OCS/alkene mixtures are shown in Table 4. The observation of reactions in C_2H_4/OCS is complicated by mass equivalences, $C_2H_4^+ = 28 = CO^+$ and $C_2H_4S^+ = 60 = OCS^+$. The reactions that can be observed and confirmed by double resonance are the formation of $C_2H_3S^+$ from $C_2H_3^+$,37, S^+,35, and OCS^+, 34, and the formation of $C_2H_2S^+$ from $C_2H_2^+$,36. Dzidic et al[2]. observed the formation of $C_2H_2S^+$ from both $C_2H_2^+$ (as found by us) and S^+. Our double resonance experiments confirm three pathways for forming $C_2H_3S^+$ whereas

the high pressure mass spectrometer study showed only one path, reaction 37
The presence of reaction 34 suggests that $\Delta H_f(C_2H_3S^+)$ as reported in
the literature[12] is too high. For propene, charge transfer from OCS^+
to the alkene is the only reaction observed.

The reactions of the butenes follow some general trends. Charge
transfer is observed in all cases, as is the formation of the $C_4H_7^+$ and
$C_3H_5^+$ ions. Formation of the latter ion is slightly endoergic and occurs
presumably through excited ionic precursors. Indeed, only at high electron
energies (50eV) is this reaction observed. The reactivity pattern for the S^+
ion is somewhat different. For 1-butene only charge transfer from S^+ is observed
while for trans-2-butene only hydride abstraction is observed. For the latter
system, the amount of S^+ is small and the double resonance signal due to the
charge transfer process may be too weak to observe. For isobutene, both
charge transfer and methide abstraction are observed.

OCS/Alkynes

The ion-molecule reactions of OCS/alkyne mixtures are shown in Table 5.
The predominant reaction of OCS^+ with acetylene is S^+ transfer leading to the
formation of $C_2H_2S^+$. Reaction of S^+ with C_2H_2 gives the products C_2HS^+ and
H. There are more reactions of OCS with $C_2H_2^+$ than of OCS^+ or S^+ with C_2H_2.
Two of the reactions of $C_2H_2^+$ are charge transfer to OCS and the abstraction
of sulfur to form $C_2H_2S^+$. The other reaction involves a transfer of H and S
between $C_2H_2^+$ and OCS leading to C_2HS^+ and HCO.

The largest number of reactions of all the hydrocarbons investigated
occurs in propyne/OCS mixtures. Charge transfer occurs from OCS^+ to propyne.
The $C_3H_3^+$ ion is formed with HS and CO as neutral products in reactions of
OCS^+ and C_3H_6,57. For this reaction to be allowed from thermodynamics, the
ion must be cyclo-$C_3H_3^+$. Both the transfer of S^+ and the transfer of S^+ with

loss of H to form $C_3H_4S^+$ and $C_3H_3S^+$ respectively are also observed for OCS^+ as the reactant ion. The S^+ ion undergoes charge transfer and formation of $C_3H_3S^+$ with loss of H. Similar reactions as those observed in acetylene occur with the hydrocarbon ions $C_3H_4^+$ and $C_3H_3^+$ to form $C_3H_4S^+$ and $C_3H_3S^+$ with loss of CO. The ion $C_3H_3S^+$ can also be formed in reactions of $C_3H_4^+$ and OCS to give HCO. The heat of formations for $C_3H_4S^+$, $C_3H_3S^+$ and C_2HS^+ are unknown and we give no values for ΔH of these reactions.

Reaction of OCS^+ with 1-butyne leads to formation of the organic ion $C_4H_5^+$ with HS and CO being the likely neutral products. The formation of $C_3H_3^+$ probably occurs from decomposition of the ion $C_4H_6^+$ formed by charge transfer from OCS^+. Again, for this pathway to be thermodynamically allowed, the cyclo-$C_3H_3^+$ ion must be formed. For S^+ reacting with 1-butyne, we note the presence of the hydride and methide abstraction reactions. Formation of the $C_4H_6S^+$ and $C_4H_5S^+$ ions is observed; however, the peaks are too small for us to determine the ionic precursors using the double resonance technique. In OCS/2-butyne mixtures, the same reactions as found for 1-butyne occur except that there is no evidence of the S^+ adduct ions $C_4H_6S^+$ and $C_4H_5S^+$. Furthermore for S^+ reacting with 2-butyne only charge transfer is observed.

These results are of interest with regard to the RF plasma experiments.[1] The presence of S atoms in the OCS plasma was examined by adding 2-butyne and n-butane as scavengers. This lead to a complicated mixture of ions. Of major importance is how ions containing C, H and S are generated. Our icr work, demonstrates that formation of organo-sulfur ions observed in the OCS/2-butyne and OCS/n-butane plasma mixtures are not likely to occur from reactions of either OCS^+ or S^+ precursor ions. Rather, it is likely that these ions are formed from reactions of hydrocarbon fragments such as

$C_2H_3^+$. Such reactions were observed in our OCS/C_2H_4 mixtures. It is also possible that ionization of neutral molecules containing both S and C is occurring in the plasma for the OCS/2-butyne mixture. This could account for the difference in the ionic mass spectra between the OCS/2-butyne and OCS/n-butane mixtures. In the latter mixture, no sulfur-organic compounds are formed from neutral S atom reactions and a much simpler ionic mass spectrum is observed.[1]

Conclusions

A variety of ion-molecule reactions of OCS have been observed in hydrocarbon mixtures. The reactions in pure OCS follow those predicted by high-pressure mass spectrometer studies. The proton affinities of CO_2, COS and CS_2 increase with substitution of S for O. The reactions in hydrocarbon mixtures can be summarized as follows: 1) Charge transfer is observed from OCS^+ when it is thermodynamically allowed. 2) Fragmentation of the hydrocarbon molecular ion after charge transfer can occur if the channel is energetically allowed. 3) Formation of a hydrocarbon ion with the neutral products HS and CO is observed in a number of systems. 4) The transfer of the CO^+ group to the hydrocarbon with formation of HS is observed, but only for CH_4 and C_2H_6. (5) Organosulfur ions are formed by the reactions of OCS^+ or S^+ with C_1, C_2 or C_3 hydrocarbons but not with C_4 hydrocarbons. Organosulfur ions can also be formed by the reaction of C_1, C_2 or C_3 organic ions with OCS.

Acknowledgement

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Table 1. Ion Molecule Reactions in Pure OCS

	Reaction	ΔH_{Rxn} (kcal/mol)
(1)	$OCS^+ + OCS \rightarrow CS_2^+ + CO_2$	-25.0
(2)	$\rightarrow S_2^+ + 2CO$	2.3
(3)	$S^+ + OCS \rightarrow S_2^+ + CO$	-52.3

Table 2. Thermodynamic Quantities Governing Proton Affinities for
          CXY(X, Y=0 or S)[a]

Molecule	Proton Affinity (kcal/mol)	Hydrogen Affinity HA(B)[d] (kcal/mol)	Ionization[e] Potential IP(B) (kcal/mol)
CO_2	126.7[b]	128.7	317
COS	168±5[c]	110±5	257
CS_2	179±3[c]	96±3	232

[a]All values in kcal/mol. The quantities are related by the expression
$PA(B) = HA(B) + IP(H) - IP(B)$ with $IP(H) = 315$ kcal/mol. Ref. 18

[b]Ref. 18.

[c]This work.

[d]Calculated from the expression in footnote a.

[e]Ref. 7.

Table 3. Ion Molecule Reactions in OCS/Alkane Mixtures

	Reaction		CH_4	ΔH_{Rxn} (kcal/mol)
4	$OCS^+ + CH_4$	$\longrightarrow$	$CH_3S^+ + HCO$	7.9
5		$\longrightarrow$	$HCS^+ + H_2 + HCO$	23.0
6		$\longrightarrow$	$CH_3CO^+ + HS$	-20.1
7	$S^+ + CH_4$	$\longrightarrow$	$CH_3S^+ + H$	-30.0
8	$OCS + CH_3^+$	$\longrightarrow$	$CH_3S^+ + CO$	-49.7
9	$OCS + CH_3^+$	$\longrightarrow$	$CH_3CO^+ + S$	-11.6
10	$OCS + CD_5^+$	$\longrightarrow$	$DOCS^+ + CD_4$	-40±5
11	$OCS + CD_4^+$	$\longrightarrow$	$DOCS^+ + CD_3$	-43±5
			C_2H_6	
12	$OCS^+ + C_2H_6$	$\longrightarrow$	$C_2H_6S^+ + CO$	-23.2
13		$\longrightarrow$	$C_2H_5CO^+ + HS$	-24.8
14	$S^+ + C_2H_6$	$\longrightarrow$	$C_2H_5^+ + HS$	-33.8
15	$OCS + C_2H_6^+$	$\longrightarrow$	$C_2H_6S^+ + CO$	-34.4
16		$\longrightarrow$	$C_2H_5CO^+ + HS$	-37.2
17	$OCS + C_2H_5^+$	$\longrightarrow$	$C_2H_5S^+ + CO$	- 6.3
			C_3H_8	
18	$OCS^+ + C_3H_8$	$\longrightarrow$	$C_3H_8^+ + OCS$	- 4.3
19		$\longrightarrow$	$i\text{-}C_3H_7^+ + CO + HS$	1.2
20		$\longrightarrow\!\!\times\!\!>$	$i\text{-}C_3H_7^+ + H + OCS$	11.6
21	$S^+ + C_3H_8$	$\longrightarrow$	$i\text{-}C_3H_7^+ + HS$	-53.4
			$n\text{-}C_4H_{10}$	
22	$OCS^+ + C_4H_{10}$	$\longrightarrow$	$C_4H_{10}^+ + OCS$	-17.0
23		$\longrightarrow$	$t\text{-}C_4H_9^+ + HS + CO$	-18.2
24		$\longrightarrow$	$t\text{-}C_4H_9^+ + H + OCS$	- 7.8
25		$\longrightarrow$	$i\text{-}C_3H_7^+ + CH_3 + OCS$	- 2.6
26	$S^+ + C_4H_{10}$	$\longrightarrow$	$t\text{-}C_4H_9^+ + HS$	-72.8
27		$\longrightarrow$	$i\text{-}C_3H_7^+ + CH_3S$	-49.7
			$i\text{-}C_4H_{10}$	
28	$OCS^+ + i\text{-}C_4H_{10}$	$\longrightarrow$	$i\text{-}C_4H_{10}^+ + OCS$	-15.0
29		$\longrightarrow$	$t\text{-}C_4H_9^+ + HS + CO$	-16.2
30		$\longrightarrow$	$t\text{-}C_4H_9^+ + H + OCS$	- 5.8
31		$\longrightarrow$	$i\text{-}C_3H_7^+ + CH_3 + OCS$	- 0.6
32	$S^+ + i\text{-}C_4H_{10}$	$\longrightarrow$	$i\text{-}C_4H_9^+ + HS$	-70.8

Table 4. Ion Molecule Reactions in OCS/Alkene Mixtures

	Reaction		C_2H_4	ΔH_{Rxn} (kcal/mol)
33	$OCS^+ + C_2H_4$	$\longrightarrow$	$C_2H_4^+ + OCS$	-12.6
34		$\longrightarrow$	$C_2H_3S^+ + HCO$	20.5
35	$S^+ + C_2H_4$	$\longrightarrow$	$C_2H_3S^+ + H$	- 1.7
36	$OCS + C_2H_2^+$	$\longrightarrow$	$C_2H_2S^+ + CO$	-42.3
37	$OCS + C_2H_3^+$	$\longrightarrow$	$C_2H_3S^+ + CO$	-14.3
			C_3H_6	
38	$OCS^+ + C_3H_6$	$\longrightarrow$	$C_3H_6^+ + OCS$	-33.0
			$i\text{-}C_4H_8$	
39	$OCS^+ + i\text{-}C_4H_8$	$\longrightarrow$	$i\text{-}C_4H_8^+ + OCS$	-45.1
40		$\longrightarrow$	$C_4H_7^+ + HS + CO$	- 5.4
41		$\left(\dfrac{\text{high } e^-}{\text{energy}}\right)$	$C_3H_5^+ + CH_3 + OCS$	5.4
42	$S^+ + i\text{-}C_4H_8$	$\longrightarrow$	$i\text{-}C_4H_8^+ + S$	-26.7
43		$\longrightarrow$	$C_3H_5^+ + CH_3S$	-40.8
			trans-2-butene	
44	$OCS^+ + C_4H_8$	$\longrightarrow$	$C_4H_8^+ + OCS$	-46.4
45		$\longrightarrow$	$C_4H_7^+ + HS + CO$	- 6.7
46		$\longrightarrow$	$C_3H_5^+ + CH_3 + OCS$	5.4
47	$S^+ + C_4H_8$	$\longrightarrow$	$C_4H_7^+ + HS$	-61.3
			1-butene	
48	$OCS^+ + C_4H_8$	$\longrightarrow$	$C_4H_8^+ + OCS$	-49.1
49		$\longrightarrow$	$C_4H_7^+ + HS + CO$	- 9.4
50		$\longrightarrow$	$C_3H_5^+ + CH_3 + OCS$	1.4
51	$S^+ + C_4H_8$	$\longrightarrow$	$C_4H_8^+ + S$	-30.7

Table 5. Ion Molecule Reactions in OCS/Alkyne Mixtures

	Reaction		C_2H_2	ΔH_{rxn} (kcal/mol)
52	$OCS^+ + C_2H_2$	$\longrightarrow$	$C_2H_2S^+ + CO$	-36.6
53	$S^+ + C_2H_2$	$\longrightarrow$	$C_2HS^+ + H$	$-307 + \Delta H_f^{\circ}(C_2HS^+)$ *
54	$OCS + C_2H_2^+$	$\longrightarrow$	$C_2H_2^+ + OCS^+$	-5.7
55		$\longrightarrow$	$C_2H_2S^+ + CO$	-42.3
56		$\longrightarrow$	$C_2HS^+ + HCO$	$-274.9 + \Delta H_f^{\circ}(C_2HS^+)$ *

			C_3H_4	
57	$OCS^+ + C_3H_4$	$\longrightarrow$	$C_3H_4^+ + OCS$	-34.0
58		$\longrightarrow$	$c\text{-}C_3H_3^+ + HS + CO$	-4.3
59		$\longrightarrow$	$C_3H_4S^+ + CO$	$-296.3 + \Delta H_f^{\circ}(C_3H_4S^+)$ *
60		$\longrightarrow$	$C_3H_3S^+ + HCO$	$-260.9 + \Delta H_f^{\circ}(C_3H_3S^+)$ *
61	$S^+ + C_3H_4$	$\longrightarrow$	$C_3H_4^+ + S$	-15.6
62		$\longrightarrow$	$C_3H_3S^+ + H$	$-298.8 + \Delta H_f^{\circ}(C_3H_3S^+)$ *
63	$OCS + C_3H_4^+$	$\longrightarrow$	$C_3H_4S^+ + CO$	$-262.3 + \Delta H_f^{\circ}(C_3H_3S^+)$ *
64		$\longrightarrow$	$C_3H_3S^+ + HCO$	$-226.9 + \Delta H_f^{\circ}(C_3H_3S^+)$ *
65	$OCS + C_3H_3^+$	$\longrightarrow$	$C_3H_3S^+ + CO$	$-250.3 + \Delta H_f^{\circ}(C_3H_3S^+)$ *

			$1\text{-}C_4H_6$	
66	$OCS^+ + 1\text{-}C_4H_6$	$\longrightarrow$	$C_4H_6^+ + OCS$	-61.6
67		$\longrightarrow$	$C_4H_5^+ + HS + CO$	-14.9
68		$\longrightarrow$	$C_3H_3^+ + CH_3 + OCS$	-7.1
69	$S^+ + 1\text{-}C_4H_6$	$\longrightarrow$	$C_4H_6^+ + S$	-43.2
70		$\longrightarrow$	$C_4H_5^+ + HS$	-69.5
71		$\longrightarrow$	$c\text{-}C_3H_3^+ + CH_3S$	-53.3

			2-butyne	
72	$OCS^+ + C_4H_6$	$\longrightarrow$	$C_4H_6^+ + OCS$	-57.1
73		$\longrightarrow$	$C_4H_5^+ + HS + CO$	-10.4
74		$\longrightarrow$	$c\text{-}C_3H_3^+ + CH_3 + OCS$	-2.6
75	$S^+ + C_4H_6$	$\longrightarrow$	$C_4H_6^+ + S$	-38.7